

## Determination of vanadium in Natural gas using graphite furnace atomic absorption spectrometry (GFAAS)

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### الخلاصة

يعتبر الفناديوم اكثر الفلزات توفراً في النفط الخام ولهذا السبب يتوقع وجوده في الغاز الطبيعي المصاحب للنفط كعناصر نزره بتراكيز جزء بالبليون أو أقل. ولغرض الحصول على هذه تراكيز من الفناديوم في الغاز الطبيعي تم استخدام وسط حامضي مخفف كوسط ممتاز، ثم تم التعامل مع المحلول كنموذج لتقدير تركيز الفناديوم بواسطة تقنية طيف الامتصاص الذري بالفرن الكرافيتي. حيث أُعتبر هذه التقنية مناسبة لهذه الدراسة لتقدير الفناديوم. تم استخدام درجة حرارة الترميد 1100 °م وحرارة التذرية 2700°م على التوالي كبرنامج حراري لتقدير الفناديوم، حد الكشف المستخدم لهذا الغرض كان بحدود 0.44 مايكروغرام/لتر والكتلة المميزة هي 67 بيكوغرام والعلاقة الخطية لمنحني المعايرة تتراوح بين (40-120) مايكروغرام/لتر ومعامل الارتباط هي 0.9985 والانحراف القياسي النسبي RSD% هي (0.83-6.13)، كما تم قياس دقة هذه الطريقة من خلال قياس تركيز الفناديوم بحدود 5-10 نانوغرام \ لتر من الغاز الطبيعي والمحضر من المحلول الام حديثاً كمجهول.

### ABSTRACT

Vanadium is recognized worldwide as the most abundant metallic constituent in petroleum, and this led to expect of its existing in natural gas that associated with oil as a trace amount in ppb concentration or less. For capturing the trace amount of vanadium in natural gas we used diluted acidic medium as adsorption collection, and using the collection medium as a sample. Graphite furnace atomic absorption spectrometry (GFAAS) is the analytical method that utilized in this study to determine (nano-partical) of vanadium. The pyrolysis and atomization temperature used were 1100°C and 2700°C , respectively. This procedure allows determination of vanadium with a detection limit about 0.44µg/L and characteristic mass of 67 pg, the calibration graph was linear in the range (40-120)µg/L with correlation coefficient of 0.9980,

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and the relative standard deviation RSD% was (0.83-6.13). the accuracy of this procedure was confirmed by the determination of vanadium in a newly prepared standard solution as unknown concentration. The range of vanadium amount in natural gas supposed to be from 5-10 ng/L .

**Keyword :** determination of vanadium, adsorption collection medium, GFAAS, chemical modifiers.

## INTRODUCTION

Vanadium is one of the important metal that received extensive attention for determined it in the natural gas, as well as of its determination in crude oil since it is most abundant metals in petroleum and has been evaluated carefully in order to reduce problems during the industrial production process, since it is a catalyst poisoning and causes corrosion<sup>(1)</sup>. Vanadium in trace amount at  $\mu\text{/L}$  levels represents as essential element for normal cell growth, but it can be toxic when present in higher concentration<sup>(2)</sup>. The threshold limit values (TLV) reported are 0.5 mg/cubic meter of air. The amount of vanadium in excess of the TLV value is reported to cause dangerous diseases, so the determination of vanadium in environmental and biological sample is highly desirable<sup>(3)</sup>. The vanadium concentration in natural gas proposed to be in ng/liter. Collecting and detecting the trace element in natural gas cannot be achieved owing to the limits of sampling and detection methods<sup>(4)</sup>. When conducting the ecological geochemistry evaluation of the important natural gas fields, adsorption collection for geogas survey is introduced by researchers for the first time to collect the trace elements in the natural gas, and vanadium was found out successfully as trace elements<sup>(5)</sup>.

A recently published review presents several methods for determination of vanadium in crude oil and petroleum products, such as inductively coupled plasma (ICP)optical emission spectrometry<sup>(6)</sup>, ICP mass spectrometry<sup>(7)</sup>, X-ray fluorescence spectroscopy<sup>(8)</sup>, and even high-performance liquid chromatography with UV detection<sup>(9)</sup>. By using the technique of graphite furnace atomic absorption which is offering advantages over other techniques since the results from a simple dilution with acidic medium-solvent and ashing were found to be identical <sup>(10,11)</sup>. Stability of metal concentration in sample and calibration solutions might became a serious problem under this conditions<sup>(12,13)</sup>.The use of modifiers became an essential part of electrothermal atomic absorption spectrometry (ETAAS). Modifiers were used in essence since the early days in an effort to gain better control of the conditions in ETAAS. The main purpose of a modifier was at that time and is still today , to bind the analyte element (chemically or physically) in a form so that high enough pyrolysis temperatures could be used in order to remove the bulk of the

matrix by volatilization or decomposition prior to the atomization of the analyte element<sup>(14)</sup>.

### EXPERIMENTAL PART

#### 1- Apparatus:

All measurements in this work were carried out using Varian AA240FS graphite furnace atomic absorption spectrometer ( Mulgrave, Australia) equipped with a Varian GTA120 Atomizer unite and Varian programmable sample dispenser PSD 120 auto sampler was used for introduction of the solutions. Halo cathode lamp for vanadium furnished by Varian were used as a radiation sources, with a current of 20mA. The main analytical line at 318.4nm were used for all determination with a spectral band width of 0.2nm . deuterium lamp were used as background correction. All experiments were carried out using pyrolytically coated graphite tube without platform (partition tube coated-GTA made in Germany). Argon 99.999% was used as the purge gas with flow rate 3L/min during all stage except during atomization, were the flow was stopped. Peak height was used exclusively for signal evaluation and quantification . The optimized graphite furnace temperature program used for all determination is given in table 1. In case when chemical modifier was used, the modifier solution was introduced first, and the dry steps of the temperature program were executed in order to dry and “condition” the modifier. Then the program was stopped and the furnace allowed cooling before the sample was introduced, and the entire temperature program executed. *The* system were controlled by SpectrAA software program from Agilent Technologies installed on window XP operating system.

**Table 1. graphite furnace temperature for the determination of vanadium.**

Step	Temp (°C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
Dry	85	5	3	Normal	No	No
	95	25	3	Normal	No	No
	120	10	3	Normal	No	No
pyrolysis	1200	5	3	Normal	No	No
	1200	1.7	3	Normal	No	No
	1200	2	3	Normal	No	No
cooling	200	8.8	3	Normal	No	Yes
	200	2	0	Normal	Yes	Yes
atomization	2700	1.2	0	Normal	Yes	Yes
	2700	2	0	Normal	Yes	Yes
	2700	2	3	Normal	No	Yes

2- Reagents:

Analytical grade reagents were used throughout. Distilled deionized water (DDW) with a specific resistivity of 0.07  $\mu\text{S}/\text{cm}$ , from Milli-Q water purification system (TKA smart2pure, made in Germany) was used for the preparation of standards. All containers and glasses were soaked in 10% nitric acid for at least 24h and rinsed three times with DDW before use. The aqua stock solution of vanadium (1000mg/L) was prepared from ammonium monovanadate in 0.5mol/L nitric acid (Density = 1.01g/cm<sup>3</sup>) the working standards were prepared by serial dilution of the stock solution with DDW. Chemical modifiers are illustrated in table 2.

**Tabel 2. Details of chemical modifier**

<i>matrix modifier</i>	<i>Concentration</i>	<i>Dissolved in</i>	<i>Manufacture</i>
Palladium as Pd(NO <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O	1000 ppm, 3000 ppm	5M HNO <sub>3</sub>	BDH
Magnesium nitrate Mg(NO <sub>3</sub> ) <sub>2</sub> .6 H <sub>2</sub> O	2000 ppm	0.6M HNO <sub>3</sub>	Merck
Palladium/magnesium nitrate	3000ppm Pd/2000ppm Mg(NO <sub>3</sub> ) <sub>2</sub>	5M HNO <sub>3</sub>	BDH /Merck
L-(+)-ascorbic acid powder	10000 ppm	Deionized water	Merck

3- Preliminary analysis of the detection result of trace element in natural gas

Figure 1 shows schematic diagram of collection installation of natural gas that installed in one of the feed gas point (natural gas) in production unite related to North gas company/Kirkuk city/Iraq, which has 406 psi pressure of natural gas separated from *all* condensate that associated with the natural gas. The system is consist of 1200 psi regulator to control the high pressure of natural gas and it supported by Millipore filter to prevent coarse particles passing through the regulator followed by flow meter that controls the flow rate of the gas in the rate of 1.5L/min through the adsorption liquid (3% nitric acid). Diluted nitric acid 3% prepared from concentrated nitric acid (Wagtach, 1.42gm/L) with ultrapure water. Nitric acid was favored over other liquid medium as it collected the elements well, is easy to purify and is an ideal medium for analysis directly by GFAAS which make detection more reliable and avoid the annoying digestion previously used for solid collector<sup>(15,16)</sup>, one liter nitric acid was distributed in three glass scrubbers so that it could capture as much as possible amount of vanadium particles. After the scrubbers there is second flow meter supported with a counter to calculate

the whole volume of natural gas in liter passing through the system, here the total quantity is 1200 liter of nature gas through the liquid medium. Each unit links with clear polyvinyl laboratory tube.

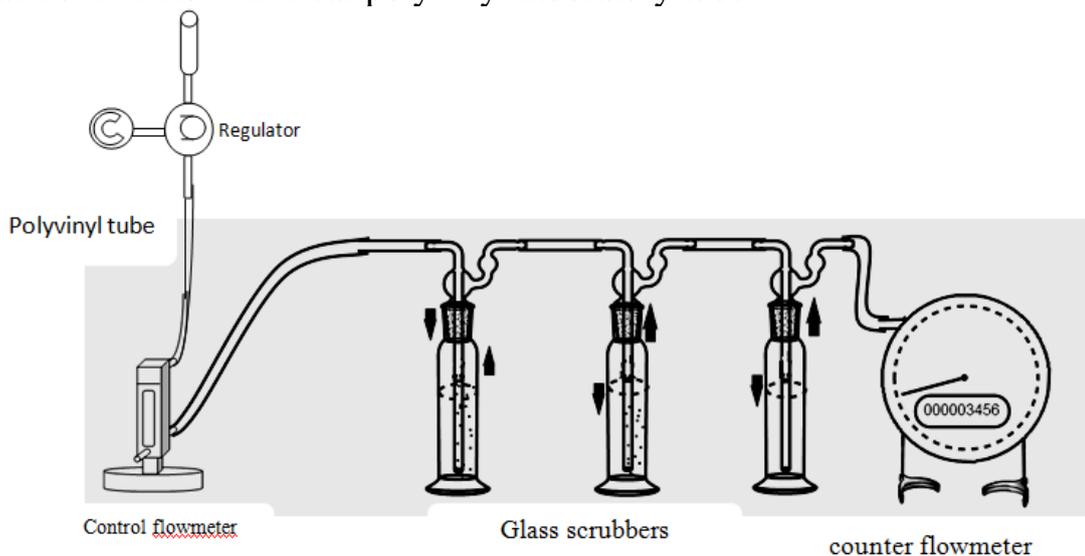


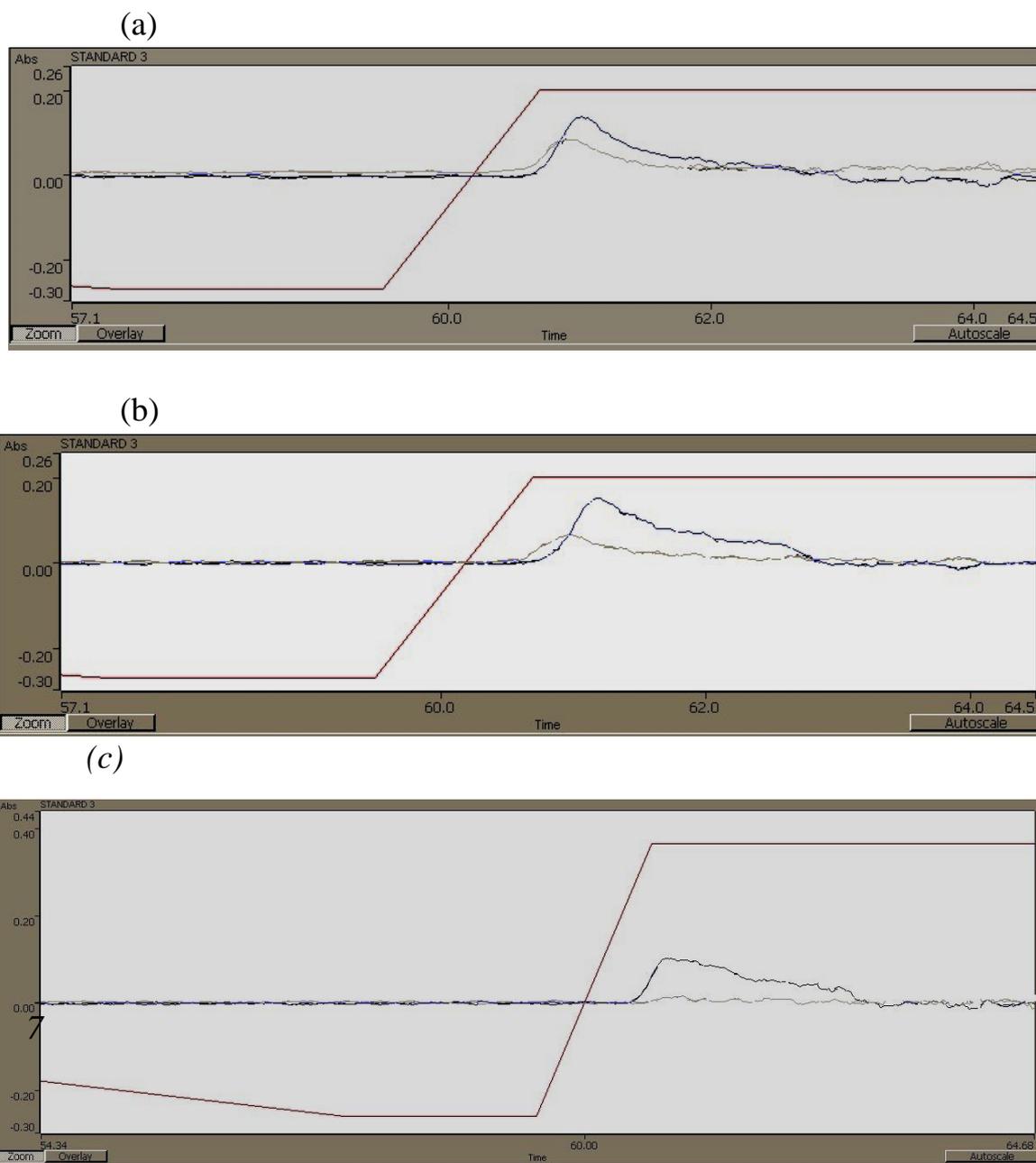
Figure 1. schematic diagram of collection installation of natural gas.

### CHEMICAL MODIFIERS

Three kinds of chemical modifiers were used to choose the maximum permissible pyrolysis temperature, magnesium nitrate has been proposed as a modifier for vanadium<sup>(17)</sup>. By using this modifier with volume equal to the sample volume, 15 $\mu$ l of magnesium nitrate with 15 $\mu$ L of the sample. 2ml ascorbic acid (10g/L) added to 10ml of the sample throughout as reduced agent. By using this two modifiers the results were not desirable, magnesium nitrate, shows relatively low signals comparing with Palladium.

Palladium has also been proposed as chemical modifier for vanadium<sup>(19,20,21)</sup> because it has been used successfully for a large numbers of elements. 15 $\mu$ L of the Palladium solution was dispensed into the graphite tub, followed by 15 $\mu$ L of the vanadium solution, calibration curve were constructed by standard solution containing (40,60,80,100 and 120ppb vanadium stock solution).

By using the mixture of equal volume of both palladium modifier 3000  $\mu$ g/L and magnesium nitrate 2000  $\mu$ g/L the results were reasonable and the mixture modifier solution could be reliable, figure 2. Shows the signal graphics for 120 ppb vanadium stock solution when using modifier in the previous three state mentioned.

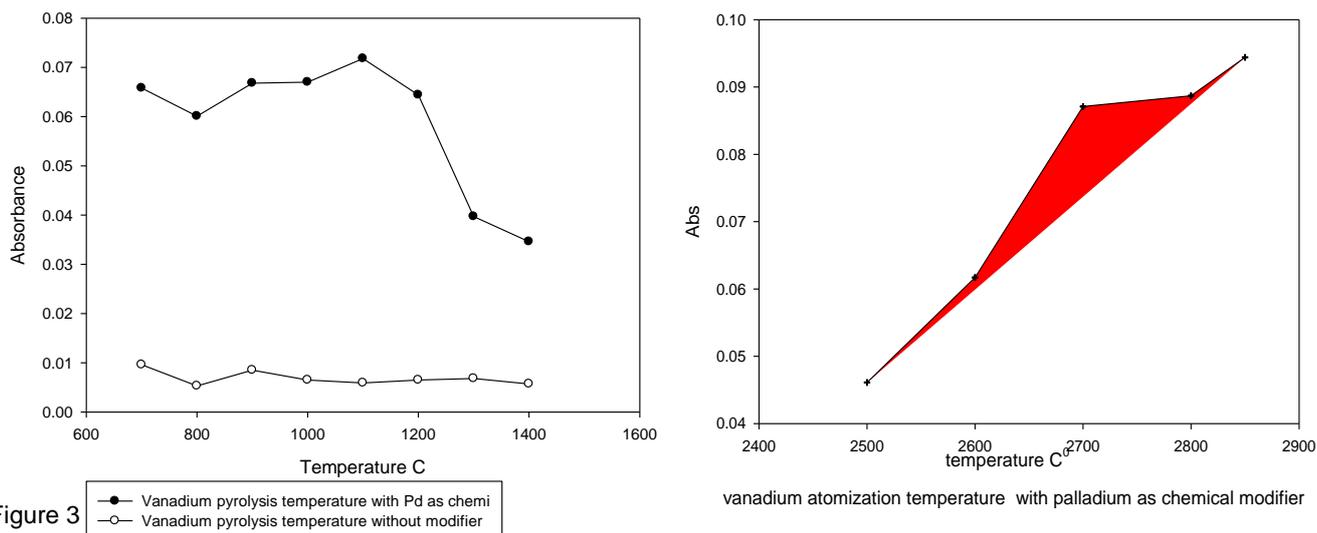


**Figure 2. (a) signal graphic for 120ppb vanadium with Palladium modifier, (b) with mixture modifier (Palladium+Magnesium nitrate ) and (c) with magnesium nitrate .**

## **RESULTS AND DISCUSSION:**

### **1-Pyrolysis and atomization temperature**

The pyrolysis and atomization temperature curves are illustrated in figure 3 those constructed by using 15 $\mu$ L vanadium standard solution 80ppb and using palladium nitrate as modifier solution. In case of absence chemical modifier more than 70% of the total concentration could be lost, this was investigated by injecting 80ppb vanadium standard solution and the instrument reading was just 25ppb.



**2- Figure of merits:**

A linear calibration graph was obtained (figure 4) for concentrations (40-120)µg/L vanadium stock solution in the presence of Pd modifier, the detection limit of vanadium was found about 0.44µg/L. the calibration graph has correlation coefficient of 0.9985 and relative standard deviation RSD% between (0.83-6.13) table 3..

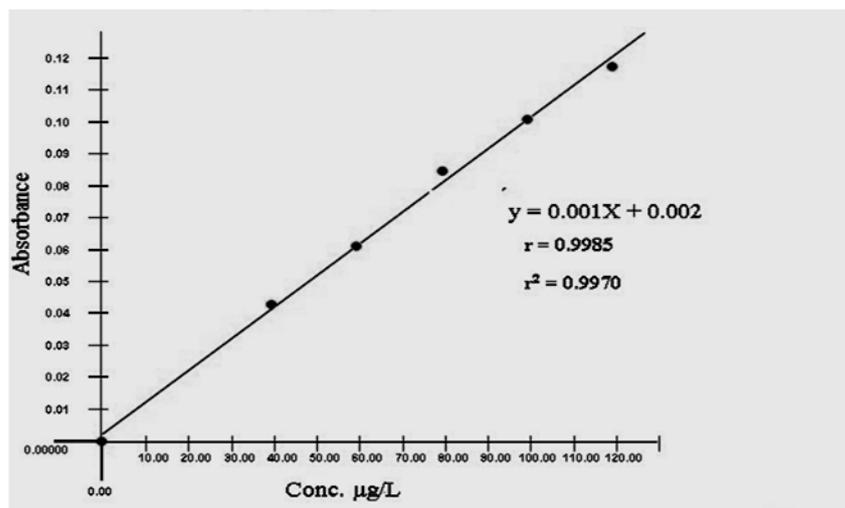


Figure 4. calibration curve for vanadium

table 3: analytical characteristics of vanadium calibrant solution for the proposed method.

Species	Values
Calibration	Absorbance = 0.001(±0.000028) [V] + 0.002 (±0.0022)
Linear analytical range (µg/l)	0.44-120 µg/l
RSD% N=3	(0.83-6.13)%
LOD (µg/l)	0.44

[V] expressed in  $\mu\text{g/l}$ ; N number of measurements

Table 4 is the summarized of the accuracy and precision of the method.

**Table 4: accuracy and precision of the method**

Conc. ppb	Abs in 3 replicate	RSD%	Erel%	%recovery
40	0.0423 0.0452 0.0400	6.13	7.00	107
60	0.0582 0.0610 0.0633	4.20	2.21	102.2
80	0.0840 0.0833 0.0847	0.83	5.6	105.6
100	0.0995 0.0986 0.1020	1.76	0.93	100.93
120	0.1172 0.1160 0.1152	0.87	-2.5	97.5

t-calculated at confidence level 95% = 1.23

t- tabulated at confidence level 95% = 4.3

the analytical condition is illustrated in table 5.

**Table 5: analytical condition for vanadium determination.**

Calibration Mode:	Concentration
Measurement Mode:	Peak Height
Wavelength:	318.5 nm
Slit Width:	0.2 nm
Lamp Current:	20.0 mA
Background Correction:	BC On
Calibration Algorithm:	Linear Origin

The correlation coefficient R and characteristic mass in pigogram obtained for vanadium using standard solution in 80ppb concentration and characteristic concentration in  $\mu\text{g/L}$  for all assays that deal with previous chemical modifiers, are given in table 6. The precision expressed as the relative standard deviation of three replicate determinations of the stock solution , prepared sample contain 7.50ng/L vanadium as average.

**Table 6. Analytical figure of merits for determination of V in natural gas**

Analyte	Modifier	R	m°(pg)	Characteristic concentration µg/L
<b>Vanadium stock solution</b>	<b>Pd + ascorbic acid</b>	<b>0.9980</b>	<b>67.6</b>	<b>4.429</b>
<b>Vanadium stock solution</b>	<b>Mg(NO<sub>3</sub>)<sub>2</sub>+ascorbic acid</b>	<b>0.9991</b>	<b>87</b>	<b>5.433</b>
<b>Vanadium stock solution</b>	<b>Pd+ Mg(NO<sub>3</sub>)<sub>2</sub>+ascorbic acid</b>	<b>0.9996</b>	<b>57</b>	<b>0.924</b>

m°: Characteristic mass

The absorbance reading for 15ul sample prepared by passing 1200 liter natural gas in 1 liter diluted nitric acid, and with the use of Pd/ ascorbic acid and the concentration for every signal is illustrated in Table 6. The amount of vanadium supposed to be in 3% nitric acid is approximately 2µg/L.

**Characteristic concentration:** this term is expressed as the concentration of an element in milligrams per liter (mg/L) required to produce a 1% absorption (0.0044 absorbance) signal.

$$\text{Char Conc. (mg/L)} = \frac{\text{Conc. of Std. (mg/L)} \times 0.0044}{\text{measured absorbance}}$$

**Characteristic mass(m:** The mass in pigogram of the analyte element producing an integrated absorbance of 0.0044 signal, it's theoretical calculation of sensitivity.

Table 7. *Vanadium concentration for the samples after passing 1200 liter natural gas.*

Concentration µg/L	Abs
8.00	0.0050
8.96	0.0088
12.1	0.0121
14.3	0.0140

So the amount of vanadium in one liter of natural gas obtained by dividing the concentrations in the table (7) by 1200 after abstracting the V amount in nitric acid is:

Vanadium concentration in ng/L of natural gas	
Maximum	10.25
Minimum	5.00
Average	7.33

## CONCLUSION

By using graphite furnace atomic absorption spectrometry with deuterium lamp background correcting it was possible to determine the nano-partical concentration of vanadium in natural gas feeds north gas company/Kirkuk city/Iraq, owing to the reason of concerning the vanadium one of refractor elements that make refractory carbides in the graphite furnace, we used pyrolytical coated tube to overcome this problem, and using appropriate chemical modifier for more sensitivity and to suppressing interferences. comparing between several kind of chemical modifiers achieved to have appropriate signals for the target.

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